

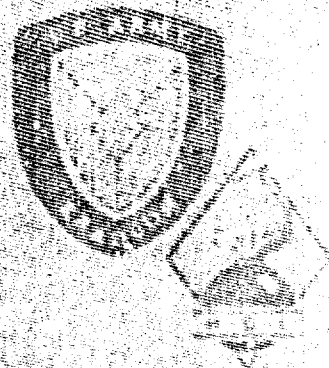
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Thermal Battery Systems for Ordnance Fuzing

by Frank C. Krieger

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U.S. Army Electronics Research
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tic/CaCrO₄ system without causing the handling and storage difficulties of the lithium systems. The calcium alloy anode should be researched to determine its capabilities in practical batteries.

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CONTENTS

	<u>Page</u>
1. INTRODUCTION.....	5
2. PRESENT THERMAL BATTERY ELECTROCHEMICAL SYSTEMS.....	6
3. ELECTROCHEMICAL SYSTEMS UNDER PRESENT INVESTIGATION FOR PROPOSED FUTURE USE.....	8
4. CALCIUM ALLOY ANODE.....	11
5. CONCLUSIONS.....	13
LITERATURE CITED.....	15
DISTRIBUTION.....	21

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1. INTRODUCTION

Thermal batteries have been used extensively in military ordnance since the early 1950's.^{1-3*} The batteries are based on fused salt electrochemical cells, examples of which have been known and investigated since 1877.⁴⁻⁸ The possible number of combinations of anode, cathode, and electrolyte materials for use in thermal cells is virtually unlimited, and many reviews of thermal batteries are available.^{3,9,10}

The number of thermal battery electrochemical systems actually used in military hardware is quite limited, however. Early investigations¹¹⁻¹³ demonstrated difficulties with many individual systems and types of systems that appear to preclude their practical use for most applications. The basic considerations used to eliminate these systems were the necessity to maximize electrical output, reliability, and storage life while minimizing cost and handling difficulties. Such eliminations were necessarily done on an empirical basis, and while they appear generally sound, a reinvestigation of some of these systems in the light of current knowledge and requirements may be helpful.

At the present time, a single electrochemical system, the Ca/LiCl-KCl eutectic/CaCrO₄ system, is used in most production thermal batteries. Other systems in use tend to be slight variations of this system with similar or slightly inferior electrical capabilities. The variations usually seen have V₂O₅, WO₃, K₂CrO₄, or PbCrO₄ in place of CaCrO₄ as a cathodic material; magnesium rather than calcium as an anode; and LiBr-KBr as an electrolyte. Specific tradeoffs available, such as long life in place of high voltage or high voltage in place of either reliability or wide operating temperature range, may make one system markedly attractive compared with others for

specific applications, particularly if factors such as availability of materials and local economic conditions are considered.

The Ca/LiCl-KCl eutectic/CaCrO₄ system has a number of desirable characteristics. Relatively high currents can be drawn over a wide operating temperature range, the LiCl-KCl eutectic is chemically stable with a high decomposition potential, and the calcium anode exhibits a high cell voltage versus CaCrO₄. Typical cell operating parameters are 2.6 V/cell at a current density of 50 mA/cm² over the temperature range of 400 to 550 C. When properly fabricated, this system is highly reliable and can be made to function for times ranging from < 1 min to ≥ 1 hr.¹⁴

It is seen, therefore, that from the virtually unlimited number of electrochemical systems available, only a handful of highly similar systems is in use. The reasons for the superior performance of these systems are poorly understood. Even for the basic Ca/LiCl-KCl eutectic/CaCrO₄ system, which has been in extensive use for more than 10 years,¹⁵ many fundamental questions remain unanswered. For example, recent termination of a CaCrO₄ manufacturing source resulted in the need to duplicate exactly that particular variant of CaCrO₄. This required an extensive research program¹⁶ that has not been entirely successful after 5 years' effort. Problems such as this emphasize the importance of the state-of-the-art approach to thermal battery technology. A cohesive empirical framework is required that can be checked continually for possible revisions as new techniques, materials, and insights become available.

Improvements in the Ca/LiCl-KCl eutectic/CaCrO₄ system appear to be possible. For example, the CaCrO₄ cathode lies about 0.6 V above the chlorine decomposition potential. Different cathodic materials that could operate closer to the chlorine decomposition potential could add up to 0.6 V/cell to the system. Two of the most serious problems with the Ca/LiCl-KCl eutectic/CaCrO₄ system at the present time are both associated with the calcium anode.

*Literature references are listed on pages 15 through 20

The first problem is the formation of CaLi_2 alloy.¹⁶ This problem is usually reduced in practical systems by the use of Le Chatelier's Principle, that is, by manipulating the concentrations of various materials (such as calcium ions in the electrolyte) in order to reduce the tendency of the alloy to form.¹⁷ When the CaLi_2 alloy (melting point, 230 C) does form at the anode surface, it forms in the molten state at the ordinary operating temperature of the thermal cell (400 to 550 C) and can flow down the cell stack and cause catastrophic short circuiting. The reason for the formation of the CaLi_2 alloy is not clearly understood, but it has been proposed¹⁸ that calcium lies above lithium in the electromotive force (emf) series in molten LiCl-KCl and the lithium simply plates out on the more electronegative calcium.

The second major problem with the calcium anode at present is the tendency to form insoluble salt films (most notably, KCaCl_3) at the calcium surface.¹⁹ This phenomenon is most serious in long life (>5 min) thermal batteries, but may affect the pulse current capabilities of even short life batteries. One of the obvious solutions to this problem is elimination of potassium ions from the electrolyte. Electrolytes in which potassium ions have been eliminated have already been used in practical batteries, but not in conjunction with the calcium anode.²⁰

The present effort in thermal battery technology to eliminate these major problems with the Ca/LiCl-KCl eutectic/ CaCrO_4 system is the use of lithium alloy anodes in the place of calcium. Alloys of lithium with boron, silicon, and aluminum have been investigated.²¹⁻²³ In addition, pure lithium has been used as the anode with proper confinement techniques.^{20,24} These anodes eliminate the CaLi_2 alloy problem entirely and permit much higher currents to be drawn without insoluble salt formation, but the high chemical reactivity of lithium results in many processing, assembly, and storage problems. The voltage of such cells has been low (typically, 1.8 V/cell at 50

mA/cm^2 over the temperature range 400 to 550 C). This voltage is low because the anodic potential of the alloyed lithium is depressed and because suitable high potential cathodes that do not interact chemically with the lithium have not been found. In addition, cell construction is inherently more complex than for the Ca/LiCl-KCl eutectic/ CaCrO_4 system, again due to the high chemical reactivity of lithium.

Because both the presently used systems and their proposed replacements show serious problems, a study was initiated to investigate these problems theoretically and empirically. This study was designed primarily to investigate the suitability of the new lithium anode thermal cells for Harry Diamond Laboratories (HDL) fuzing requirements, but other alternatives may be considered if necessary.

2. PRESENT THERMAL BATTERY ELECTROCHEMICAL SYSTEMS

The Ca/LiCl-KCl eutectic/ CaCrO_4 system is the most widely used thermal battery electrochemical system at the present time, and detailed investigations of this system date back to the middle 1950's.¹⁸ Many changes in cell construction and processing techniques have occurred since then. These have been due partly to results of studies and improvement of the basic electrochemical and processing parameters;²⁵⁻³⁰ partly to improvements in associated pyrotechnic materials, thermal insulators, and assembly techniques;^{9,15} and partly to changes in electrical requirements as fuzes evolved from vacuum tube to transistor technology. Vacuum tube technology fuzes required multiple voltages ranging from a few volts to several hundred volts and currents ranging from a few microamperes to several amperes for plate, grid, and filament voltages. These varied outputs often came from a single battery, and many ingenious geometric formulations and processing techniques were used.

Most of these techniques were proprietary, but some general examples are available.^{9,30} With the advent of transistor technology, the single voltage output battery operating at a few tens of volts at currents ranging from perhaps 100 mA to 1 A became more standard. Pulse currents of a few amperes for a few milliseconds are frequently required. In addition, lifetimes changed from less than 5 min to include required lifetimes of up to 1 hr or more.³¹ The battery design for the transistorized fuze is quite simple compared with the earlier designs and consists almost invariably of the pellet-type technology.¹⁵

In the pellet-type technology, a thermal cell with its associated pyrotechnic charge typically consists of three flat annular rings: (1) pyrotechnic heat source, (2) bimetal anode, and (3) electrolyte-cathode. This repeating unit is stacked in a series voltaic configuration simply by placing the flat annular rings on top of each other until the desired number of cells is obtained. A heat paper strip that is easily ignitable is placed in the center hole formed by the annular rings and contacts each cell from the top to the bottom of the stack. This heat paper is made from zirconium and barium chromate powders with various inorganic fibers.³² The ash is not electrically conductive, so the cells do not short-circuit. The heat paper strip ignites the main pyrotechnic heat sources, which are the flat annular rings composed of pelletized Fe/KClO₄ powder. Sufficient unreacted iron remains in the annular rings after ignition so that intercell electrical contact is made in the series stack.

The amount of pyrotechnic material is adjusted so that the cells reach their operating temperature of 400 to 550 C when fired at military ambient temperatures ranging from -54 to +74 C (-65 to +165 F). Because a fixed amount of pyrotechnic material is used for units fired at all ambient temperatures, a wide operating temperature range for the cells is desirable to permit maximum cooling time (above the freezing point of the electrolyte) at

low ambient temperature as well as to prevent overheating the cells when fired at high ambient temperature. Some heat may be stored in fusible materials melting within the cell operating temperature range to compensate for heat losses and to prevent cell overheating.^{15,33-35} Exothermic chemical side reactions within the cells themselves help to compensate for heat losses, but can also lead to thermal runaway.³⁶ The entire cell stack is thermally insulated from its environment, usually with asbestos, Fiberfrax, or more recently Min-K.^{14,37}

The bimetal anode normally consists of calcium that has been vapor deposited on mild steel or nickel. The calcium may also be mechanically fixed to an inert metal backing or simply used in sheet form. The properties and the functioning of the calcium anode have been the subject of many studies.³⁸⁻⁴⁴ The calcium must be handled in a dry room atmosphere to prevent oxidation or nitridation.⁴⁵⁻⁴⁷ The relative humidity must be less than 5 percent and preferably 1 or 2 percent. The functioning of the calcium anode is not completely understood. The generally accepted mechanism is shown below.

- | | |
|--|------------------------------------|
| (1) $\text{Ca} \rightleftharpoons \text{Ca}^{++} + 2\text{e}$ | electrochemical
anodic reaction |
| (2) $\text{Ca} + 2\text{Li}^+ \rightleftharpoons \text{Ca}^{++} + 2\text{Li}$ | chemical side
reaction |
| (3) $\text{Ca} + 2\text{Li} \rightleftharpoons \text{CaLi}_2$ (mp 230 C) | chemical side
reaction |
| (4) $\text{CaLi}_2 \rightleftharpoons \text{Ca}^{++} + 2\text{Li}^+ + 4\text{e}$ | electrochemical
anodic reaction |

The CaLi₂ of reaction (4) is believed to be the true anode of the cell. The favorable kinetics of the calcium electrode are believed to be due to the constant renewal of the fluid anodic surface as new molten CaLi₂ forms.⁴¹ A KCaCl₃ film and a more diffuse Ca₂CrO₄Cl film is formed on the surface of the calcium almost immediately after initiation,^{19,25} and these films are believed to prevent excessive chemical exothermic reaction between the calcium anode and the CaCrO₄ dissolved in the electrolyte.³ Temperatures above 550 C are

usually avoided to prevent breakdown of these films and resultant thermal runaway. Unfortunately, the anodic films continue to build during the cell lifetime in such a way that the maximum anodic capacity is typically limited to about 30 percent of the anodic material available in long life batteries.¹⁵

The third component of thermal cells in present use is the DEB electrolyte-cathode pellet. This flat annular ring comprises pelletized powders: calcium chromate depolarizer (D), LiCl-KCl eutectic electrolyte (E), and finely divided silica binder (B) that prevents flow of molten electrolyte from the cell through use of capillary action. The DEB powder is made by a series of calcining, drying, grinding, mixing, and baking procedures.⁴⁸ The DEB pellets are usually made from a homogeneous powder, but two-layer DEB pellets with no calcium chromate on the layer next to the anode also are made.

There appears to be little difference in performance between the two-layer and homogeneous DEB pellets, presumably due to the solubility of CaCrO_4 in the LiCl-KCl eutectic electrolyte.²⁷ The homogeneous DEB powder typically consists of 38-percent CaCrO_4 , 55-percent LiCl-KCl eutectic, and 7-percent SiO_2 by weight. The powder is pelletized by using forces of several tons per square centimeter. Apparent pelletized densities of 1.6 to 2.0 g/cm^3 are often used, while the maximum theoretical density, depending on the exact chemical composition, is about 2.3 g/cm^3 .

The performance characteristics of the DEB powders are highly dependent on the processing parameters, the gross chemical composition, and the type of CaCrO_4 used.^{16,49,50} Although these problems are poorly understood at present, in practice, acceptable DEB powders can usually be made through trial and error. Homogeneity of the powders on a microbasis and particle size distribution of the CaCrO_4 may be major difficulties in DEB powder processing.¹⁶ The exact mechanism of reduction of CaCrO_4 in the thermal cell is not known and probably

depends on conditions during discharge. Reduction from Cr(VI) to Cr(III) has been proposed and confirmed,⁵¹ as has reduction from Cr(VI) to Cr(V) as $\text{Ca}_2\text{CrO}_4\text{Cl}$ at low discharge rates.²⁵ Various chemical interactions between the thermal cell components are known to occur at the cell operating temperatures,⁵² and the axial stack force during discharge is known to be important.⁵³

The basic output parameters of the Ca/LiCl-KCl eutectic/ CaCrO_4 system are listed in the introduction with a brief comparison with other presently used systems. The discussion in this section should help to amplify the complex nature of the technology and suggest some of the reasons that so few electrochemical systems have been used or studied extensively for practical applications.

3. ELECTROCHEMICAL SYSTEMS UNDER PRESENT INVESTIGATION FOR PROPOSED FUTURE USE

A number of possibilities for improving the present thermal battery electrochemical systems are being investigated. These are associated with (1) lowering the cell operating temperature, (2) changing the cathodic material, (3) changing the anodic material, (4) improving processing and implementation of the basic system as it is now used, and (5) changing the electrolyte composition to eliminate troublesome species.

A great deal of information on molten salt systems is available.^{7,8,39,54-58} However, the mechanisms of cell behavior are complex and incompletely understood. Furthermore, there are various practical requirements such as (1) having good chemical stability of cell components that must also be electrochemically active, (2) operating the cell over a wide temperature range, and (3) obtaining known and reproducible electrical outputs from the cells in a research program of reasonable funding. Because of the technical complexity and the economic requirements, innovations in thermal cell electrochemistry have tended to

be conservative. Of the many electrolytes that might be chosen, for example, only the halide systems have proved practical, and almost all production thermal battery cells use only the LiCl-KCl eutectic electrolyte.⁸

Exploratory work on radically new systems has been done over the years and is continuing.^{33,59-63} Some of the most promising low operating temperature systems (175 to 275 C) are based on the NaCl-AlCl₃ electrolyte.⁶⁴ These systems have the advantage of operating at relatively low temperatures at which heat transfer considerations are minimized; also, cells can be sealed more easily for high spin applications. Cathodes of MoCl₅, CuCl₂, and FeCl₃ have been evaluated with anodes of Li/Al, Li/Si, and Li/B by using the NaCl-AlCl₃ electrolyte with a SiO₂ binder. Practical batteries that operate at 2.5 V/cell and 150 mA/cm² have been reported.⁶⁰

Difficulties with the system include an inherently narrow operating temperature range and apparent problems with reproducibility, electrical noise, and chemical stability. At present, practical units made from the NaCl-AlCl₃ electrolyte cannot be compared directly with practical units made from the Ca/LiCl-KCl eutectic/CaCrO₄ system due to lack of sufficient data on the NaCl-AlCl₃ systems. However, it appears that some sacrifice in performance could be expected in practical NaCl-AlCl₃ systems due to problems with reaction kinetics at the lower operating temperatures.⁶⁴ Other low temperature thermal battery systems investigated to date^{33,59,65} have shown slightly or significantly lower electrical outputs than the Ca/LiCl-KCl eutectic/CaCrO₄ system.

Higher temperature systems than those presently in use do not appear attractive for ordnance applications. The heat transfer and materials problems are intensified, and electrical outputs are not significantly higher for a variety of practical reasons usually involving increased chemical reactivity at the elevated temperatures.⁸

Many systems varying slightly from the basic Ca/LiCl-KCl eutectic/CaCrO₄ system are being investigated.^{63,66-68} The basic system itself has been the subject of detailed investigations for many years.^{14-16,18,69-71} Two of the most serious problems with the Ca/LiCl-KCl eutectic/CaCrO₄ system are CaLi₂ formation, which can result in cell short circuiting, and KCaCl₃ film formation, which can reduce output current. Both problems can be eliminated by eliminating the calcium anode. The most frequently investigated methods of eliminating the calcium anode at present are (1) the use of a pure lithium anode (mp 179 C) with proper confinement techniques^{3,20,24} and (2) the use of various lithium alloy anodes, which have melting points in excess of the maximum cell operating temperature of approximately 550 C.²¹⁻²³ Liquid lithium electrodes interfacing with molten salt electrolytes can support current densities as high as 5 to 10 A/cm² and demonstrate higher energy densities than similarly made lithium alloy anode batteries.³ The lithium alloy anode batteries in turn demonstrate higher energy densities than are available from similar calcium anode batteries. Energy densities of properly engineered systems using the liquid lithium anode can be as much as six times those available from the Ca/LiCl-KCl eutectic/CaCrO₄ system.

The potential of pure molten lithium versus the Pt(+2) - Pt(0) reference electrode in LiCl-KCl eutectic at 450 C is -3.41 V. For 20/80 weight percent Li/Al the potential is -3.11 V, and for 33/67 weight percent Li/Si (Li₂Si) the potential is -3.09 V versus the same reference. The total voltage span available in molten LiCl-KCl eutectic from lithium oxidation to chlorine reduction is 3.63 V.^{3,8} The potential of the calcium anode in the LiCl-KCl eutectic is difficult to define because of the CaLi₂ formation, but probably lies near the potential for pure lithium.

Sandia Laboratories of Albuquerque, NM, has investigated the lithium alloy anode approach extensively for primary thermal batteries,^{22,23,72-75} and Argonne National

Laboratory of Argonne, IL, has investigated the same approach in terms of secondary batteries for vehicular propulsion and load leveling applications.⁷⁶⁻⁸¹ The Naval Surface Weapons Center of Silver Spring, MD, has worked with lithium-boron alloys for primary thermal batteries.^{21,82,83} A number of basic studies of lithium and its alloys in molten salts are reported in the literature.⁸⁴⁻⁸⁹

The above laboratories have all used LiCl-KCl eutectic as the electrolyte and FeS₂ as the cathodic material in their batteries. Lithium has been shown to interact chemically with LiCl-KCl eutectic melts.⁸⁵ The FeS₂ cathodic material reacts vigorously with the lithium and lithium alloy anodes at elevated temperature and must be separated from the anodes with a special electrolyte-separator layer to prevent chemical reaction. A major advantage of FeS₂ as a cathodic material is that FeS₂ is insoluble in molten LiCl-KCl eutectic and, hence, cannot diffuse to the anode and cause chemical short circuiting. Unfortunately, FeS₂ is subject to thermal decomposition at elevated temperatures. Under a nitrogen atmosphere, thermal decomposition of FeS₂ was observed at temperatures as low as 400 C.³ The resultant free sulfur could be expected to react vigorously with the lithium

The lithium alloy-iron disulfide thermal cells have low cell voltages (≈ 1.8 V/cell at 50 mA/cm²). Higher cell voltages would greatly enhance miniaturization characteristics for short life applications.

To illustrate the potentialities of this type of system, some characteristics of the LiSi/LiCl-KCl eutectic-MgO/LiCl-KCl eutectic-SiO₂-FeS₂ system⁷² are described below. This system was tested extensively at the Sandia Laboratories in the form of a 28-V, 0.5-A primary thermal battery in a volume of 400 cm³ (7.6 cm in diameter and 9 cm long) with a lifetime of 50 to 60 min when fired at room temperature. The thermal insulation used was Min-K,³⁷ which is high in cost and one of the most efficient thermal battery insulators commercially available. The individual cells each

consisted of six flat discs: (1) cathodic current collector, (2) cathode, (3) electrolyte-separator, (4) anode, (5) anodic current collector, and (6) pyrotechnic heat source.

The discs were 5.1 cm in diameter, so the cell area was 20.4 cm², and the total height of each six-disc cell was 0.38 cm. The collectors (discs 1 and 5) were cut from a 304 or 321 stainless steel sheet. The cathode (disc 2) was a homogeneous pelletized powder mixture comprising 64/16/20 weight percent FeS₂/E/EB, where E is a LiCl-KCl eutectic electrolyte and EB is a separately processed mixture of 88 weight percent LiCl-KCl eutectic and 12 weight percent finely divided SiO₂. The electrolyte-separator (disc 3) consisted of a 65/35 weight percent mixture of a LiCl-KCl eutectic electrolyte and a MgO binder and also was a homogeneous pelletized powder. The MgO binder must be used next to the lithium anode, even though it is a less effective binder than the SiO₂, in order to prevent chemical reaction of the lithium alloy anode with SiO₂ at elevated temperatures. The lithium silicon anode (disc 4) consisted of a 45/55 weight percent Li/Si pelletized powder, and the pyrotechnic heat source (disc 6) consisted of 88/12 weight percent Fe/KClO₄ homogeneous pelletized powder.

For the 15-cell battery, the peak voltage was 30.6 ± 0.6 V, or 2.04 ± 0.04 V/cell across a 56-ohm load. The current was 0.5 A at 28 V or 24 mA/cm² of cell area. Lifetime and time to activation were both measured to 75 percent of peak voltage or 23 V. Activation time to 23 V was 1.4 s at -50 C, 1 s at +25 C, and 0.7 s at +75 C. Lifetime to 23 V varied from 34 min at -50 C to 38 min at +75 C with a maximum of 58 min at +48 C. Such behavior indicates a near optimal heat balance for the system. Batteries fired at temperatures of >50 C resulted in internal cell temperatures that exceeded ≈ 525 C and produced shortened cell lifetime. The reproducibility of the electrical output for this system was decidedly better than that of previous long life thermal battery systems.^{14,36,72}

A slightly larger version of this battery, still 7.6 cm in diameter, but 10.2 cm instead of 9 cm long and with slightly thicker cells,²³ was fired at room temperature at current densities ranging from open circuit to 1000 mA/cm² and gave the following peak voltages normalized to peak voltage per cell:

Current density (mA/cm ²)	Peak voltage (V)
Open circuit	2.17
25	2.00
50	2.00
75	1.93
150	1.87
500	1.67
1000	1.56

A voltage spike on initiation of 0.2 V/cell was observed at open circuit. At current densities ranging from 25 to 75 mA/cm², the voltage spike was 0.1 V/cell; at current densities of 150 mA/cm² and above, the voltage spike was insignificant. This initial voltage spike is characteristic of the system and is believed to be associated with surface impurities in the FeS₂ cathode.⁷⁵

While the battery was operating at its normal rate (24 mA/cm²), pulse currents were drawn through a 1-ohm resistive load. The pulses were applied at 60-s intervals and were of 90-ms duration. Pulse currents were above 1200 mA/cm² with 5-V polarization (such as 29 to 24 V), and recovery to the original voltage was rapid.⁷² This level far exceeds the pulse capabilities of the Ca/LiCl-KCl eutectic/CaCrO₄ system, in which pulse currents of 120 mA/cm² often result in severe polarization, depending on the operating conditions and the processing techniques.⁶⁹ Batteries operating under a continual heavy load showed good performance. The nominal 500-mA/cm² batteries operated at 8 A for approximately 10 min.

The performance data above indicate a reliable, high current and energy density system. The high chemical reactivity of lithium and its alloys will cause many problems and increase costs, but the problems do not appear insoluble. The miniaturization of the system for short life applications (< 5 min) has not been demonstrated.

4. CALCIUM ALLOY ANODE

The preceding sections should help to exemplify the experimental complexity of thermal cell electrochemistry and demonstrate the reasons for the severe limitations on the number of electrochemical systems that have been successful. The basic problem is kinetics. Materials must be found that are electrochemically active over a wide operating temperature range (400 to 550 C), yet chemically stable over the same range as well as at lower temperatures encountered during storage (-54 to +74 C) for extended periods (25 years) and that can be fabricated at ordinary room temperature without prohibitively expensive environmental control.

The kinetics of chemical reactions can be influenced to a marked degree by catalytic agents, local temperature changes, local surface conditions, impurity types and amounts, and other similar factors so that accurate prediction of reaction rates is difficult. For example, rates of reactions between metals and gases, an important consideration for storage and handling, have been reported to differ by a factor of seven by the same investigators using identical experimental techniques.^{45,90,91} The problem of obtaining CaCrO₄ that shows reproducible electrochemical kinetic behavior has already been mentioned.^{16,70} In the absence of a comprehensive theoretical or empirical framework, deviations from proven systems such as Ca/LiCl-KCl eutectic/CaCrO₄ must be considered carefully; radically new systems are almost certain to require many

years of research and development before they are adequately characterized.

The major improvements that could be made on the most successful electrochemical system to date, the Ca/LiCl-KCl eutectic/CaCrO₂ system, are the elimination of CaLi₂ (mp 230 C) formation, which can cause electrical short circuiting during operation, and the elimination of KCaCl₃ formation, which limits current and coulombic capacity. The proposed new systems based on lithium or lithium alloy anodes do, in fact, eliminate these problems but show low cell voltages, greater cell complexity, and more processing and storage problems due to the high chemical reactivity of lithium.

The use of anodes made from calcium alloys might eliminate the major problems of both the present pure calcium anode system and the proposed lithium anode systems. The rate of formation of CaLi₂ could be reduced to an acceptable level by Le Chatelier's Principle simply by reducing the amount of calcium in the anode. It is also possible that CaLi₂ formation might be eliminated completely by use of calcium alloy anodes of lower free energy than pure calcium in the LiCl-KCl melt,^{40,86,92,93} although some CaLi₂ may be necessary for proper cell operation.⁴¹ Lithium alloy anodes have been shown to function properly over a wide range (≈80 percent) of chemical composition in thermal cells.^{23,86,87} Diffusion of calcium through the solid alloy will be less than for lithium, but formation of molten CaLi₂ should aid in calcium transport. Operation over a wide composition range is essential for long life alloy anodes as active material is consumed. At present, most HDL fusing applications use only 2 to 5 percent of the available anodic material, so this problem should be minimal.

Unfortunately, a purely theoretical study of the alloy anode problem is severely limited because of the difficulty of defining the actual mechanisms involved and the actual experimental conditions under which they occur.

For example, the oxidation potential of calcium in LiCl-KCl eutectic has been postulated to lie above that of lithium in order to account for CaLi₂ formation,¹⁸ while calculations from the free energies of the halides of the corresponding metals indicate that the oxidation potential probably lies below the lithium potential.^{8,94} The exact anodic reaction mechanism is simply not known. In most attempts to define an experimental emf series in molten LiCl-KCl eutectic,^{8,95} calcium is omitted, regardless of its great importance in thermal cell electrochemistry.

Although the limitations of theoretical calculations must be recognized, it must also be remembered that intelligent application of theory to well-defined situations can permit the legitimate exclusion of large areas of experimental work that might otherwise appear necessary. Phase equilibria and other data on many alloys⁹⁶⁻⁹⁸ and molten salt systems^{7,8,39,54-58} necessary for such calculations are available. Thermodynamic properties of the calcium alloy anodes can be calculated from emf data.^{86,99-104} Other methods include partial pressure measurements, equilibrium measurements of exchange reactions, and thermodynamic evaluation of the phase diagrams.^{40,93,105} Metals that form alloys with calcium melting above 600 C might be suitable for the calcium alloy anode:

Aluminum	Manganese
Barium	Silicon
Bismuth	Strontium
Cadmium	Thallium
Copper	Tin
Indium	Titanium
Lanthanum	Zinc
Lead	

Factors such as cost, chemical reactivity, and toxicity must be considered when metals are selected for experimentation.

These molten salt eutectics would exclude potassium ions in order to permit larger current drain than at present.⁷

$\text{CaCl}_2\text{-LiNO}_3$	mp 320	C
LiCl-LiF-LiI	mp 341.1	C
$\text{LiCl-Li}_2\text{CrO}_4$	mp 350	C
LiBr-LiI-LiCl	mp 357	C
LiBr-LiF-LiI	mp 367	C
LiCl-LiI	mp 368.3	C
$\text{LiBr-Li}_2\text{CrO}_4$	mp 370	C
LiCl-PbCrO_4	mp 388	C
LiCl-PbCl_2	mp 400	C
LiF-LiI	mp 411	C
LiBr-LiCl-LiF	mp 430	C
LiBr-LiF	mp 448	C
LiF-RbF	mp 450	C

This list is not meant to be inclusive, but to illustrate the number of systems that have lithium ions available for some CaLi_2 formation if necessary and at the same time have no potassium ions, a low melting point, and chemical similarity to the present LiCl-KCl eutectic- CaCrO_4 electrolyte-cathode system. Many descriptions are available of reference electrodes and electrochemical measurement techniques required for working with the above types of molten salt systems.¹⁰⁶⁻¹⁰⁸

The basic intent in introducing the calcium alloy anode is to eliminate cell short circuiting due to CaLi_2 (mp 230 C) formation. If the anode is used with electrolytes that do not include potassium ions, larger currents might be drawn than at present since KCaCl_3 films cannot form. If successful, such systems would solve the major problems of the present pure calcium anode systems and, in addition, retain the advantages of the pure calcium anode systems of high cell voltage, construction simplicity, and ease of handling without introducing the problems of chemical reactivity, low cell voltage, handling difficulties, and cell and processing complexity associated with the pure lithium and lithium alloy anode systems. Much of the work done during the past 25 years on the Ca/LiCl-KCl eutectic/ CaCrO_4 system would still apply since the change in the system is minimal, and the anode materials problems should be eased slightly since the chemical reactivity of the alloyed calcium should be less than that of pure calcium. Future work on improved cathodic materials

would be enhanced by any decrease in chemical reactivity of the alloyed calcium.

5. CONCLUSIONS

The Ca/LiCl-KCl eutectic/ CaCrO_4 system presently used in thermal battery ordnance applications has been used extensively and successfully for many years. The major problems with this system are CaLi_2 formation, which can cause cell short circuiting, and KCaCl_3 film formation at the anode, which limits current and coulombic capacity.

Proposed new systems such as LiSi/LiCl-KCl eutectic- MgO/LiCl-KCl eutectic- $\text{SiO}_2\text{-FeS}_2$ eliminate both major problems of the Ca/LiCl-KCl eutectic/ CaCrO_4 system, but introduce new problems of low cell voltage, cell and processing complexity, and handling and storage difficulties. Most of these problems are caused by the high chemical reactivity of lithium. The miniaturization of lithium anode cells has not been demonstrated.

A calcium alloy anode system used in conjunction with molten salt electrolytes that do not contain potassium ions may be an alternative solution to both major problems of the Ca/LiCl-KCl eutectic/ CaCrO_4 system. The calcium alloy anode would not cause the problems related to chemical reactivity that the lithium or lithium alloy anodes cause; material problems might be eased slightly if the calcium alloy were less reactive than pure calcium. The calcium alloy anode system is a small variation from the present pure calcium anode system, and its use permits application of many previously proven materials and techniques. Operation of calcium alloy anodes over a wide range of calcium composition has not been demonstrated.

Because of their proven capabilities, the lithium and lithium alloy anode systems should be investigated in terms of a development fuzing program. Particular attention should be paid to the miniaturization of these systems. The calcium alloy anode systems should be researched.

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